

## CHEMICAL AND ISOTOPIC COMPOSITION OF CARBONATES IN RECENT SEDIMENTS AND SOILS FROM WESTERN EUROPE<sup>1</sup>

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**ABSTRACT:** The sediments and soils constitute an erosion-sedimentation cycle composed of: Solid carbonate rock → Soil → Fluvial sediment → Estuarine sediment → Marine sediment → Salt marsh. Determinations were made of the total carbonate and dolomite contents of the sediments as well as the strontium and carbon-14 content of the carbonates and their stable carbon and oxygen isotopic composition. In soils the isotopic composition of the carbonates was studied. The soils analysed are from the Netherlands and France. The sediments are from the rivers Rhine, Meuse, Ems, Seine, Somme and Rhône, from the estuaries of the Rhine, Meuse and the Ems and from the coastal areas of Belgium, the Netherlands and Western Germany.

The isotopic composition of the carbonates in soils is different from that of the parent material. This difference is due to the presence of newly formed carbonates. The amount varies between 10 and 50% of the carbonates present. The rivers Rhine, Meuse and Seine contain both soil-derived carbonates and carbonates from eroded carbonate rocks. The carbonates in the river Somme originate mainly from carbonate rocks. The carbonates in the estuaries of the Rhine, Meuse and Ems are predominantly derived from the marine environment. The carbonates are transported up to the freshwater boundary in these estuaries. The carbonates in marine sediments from the Wadden area are derived for about one fifth from the rivers Rhine and Meuse.

### INTRODUCTION

Carbonate rocks occur rather abundantly on the continent of Western Europe. Carbonate particles are washed away from the soils developed on these rocks and added to the sediment load of the rivers. The carbonate content of the river deposits investigated varies between 2 and 40%. The bulk of this material is transported by way of the estuaries to the North Sea. There the fluvial carbonates are added to carbonates derived from skeletal material and from eroded carbonate formations along the coast.

The marine sediments are transported by the prevailing currents to the various areas of deposition. An important depositional area is the Wadden Sea in the Northern part of the Netherlands and Western Germany (localities 9-13 in Fig. 1). When the accumulation of the tidal sediments has reached the mean high water

level, it is possible for plants to settle and the tidal flat is turned into a salt marsh. The sediments and soils discussed are all part of the same erosion-sedimentation cycle.

The object of this investigation was to study the origin of the carbonates in this cycle by means of mineralogical, chemical and isotope analysis. Weathering processes were studied in soils on carbonate rocks and salt marshes. More than 1,200 sediment samples were collected at the localities shown in Figure 1. Samples are partly from the same set as used by de Groot (1964) for his manganese study, additional samples have been taken in the course of this investigation.

### EXPERIMENTAL METHODS

#### *The Total Carbonate Content of the Sediments and Soils*

The total carbonate content was measured by treating the sample with dilute hydrochloric acid solution and the carbon dioxide evolved is measured by gas volumetry. This amount is converted to the percentage calcium carbonate in the sample.

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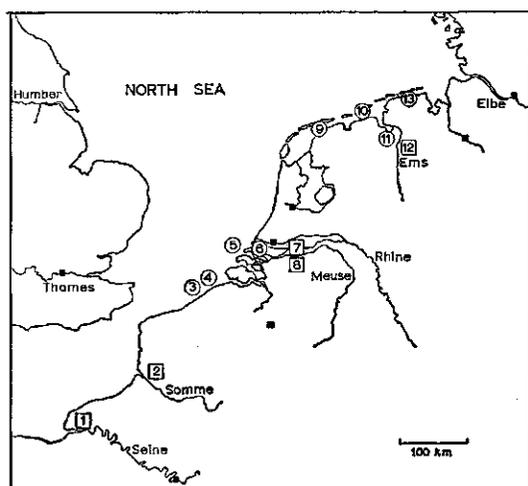


FIG. 1.—The area studied. Detailed maps of the Rhine-Meuse estuary and the Ems estuary are given in Figures 7 and 9.

- |                    |                    |
|--------------------|--------------------|
| 1 = Seine          | 8 = Meuse          |
| 2 = Somme          | 9 = Friesland      |
| 3 = Vlaamse Banken | 10 = Groningen     |
| 4 = Zwarte Polder  | 11 = Dollard       |
| 5 = Grevelingen    | 12 = Ems           |
| 6 = Haringvliet    | 13 = Ost-Friesland |
| 7 = Rhine          |                    |

#### The Carbonate Content of Samples at Separate Localities

The carbonates in the investigated sediments occur mainly in the silt-sized fraction. The carbonate content of sediment samples from the same locality may show a wide range of values. In sandy samples the carbonate content is lower compared to that of the clay-rich samples. Therefore, in comparing different sedimentation areas, samples with the same grain-size distribution have to be compared. As a measure of the grain-size distribution in these finely grained sediments, we use the percentage of particles with a diameter less than  $20 \mu\text{M}$ . To compare the carbonate content between different areas we use the carbonate content at 50% less than  $20 \mu\text{M}$  (Fig. 2). These values are obtained by analysing from each separate locality a large number of samples and constructing curves as shown in Figure 2.

#### Mineralogy

The mineralogy was determined by X-ray diffraction analysis. Use was made of a Philips diffractometer,  $\text{CuK}\alpha$  radiation was employed. A monochromator was mounted in front of the counter; this eliminated background radiation

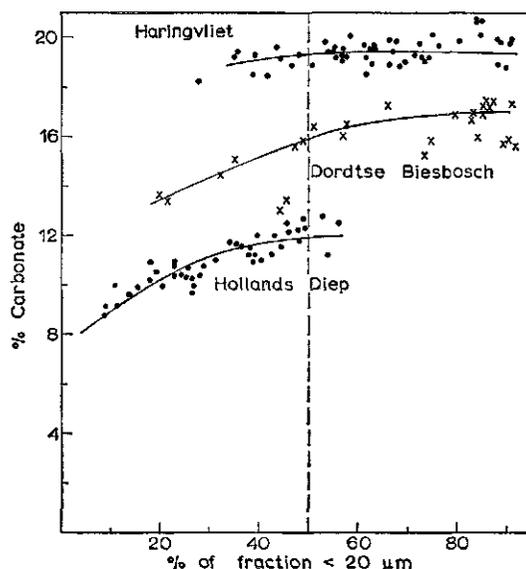


FIG. 2.—Relationship between the total carbonate content and the percentage of particles less than  $20 \mu\text{m}$  in sediment samples from the Hollands Diep, Dordtsche Biesbosch and Haringvliet. For comparison the carbonate content at  $50\% < \mu\text{m}$  is used.

due to the fluorescence of iron present in the sediment samples.

The magnesium content of calcite was estimated from the position of the 104 reflection (Goldschmidt *et al.*, 1961). Fluorite was used as an internal standard. In a few cases the magnesium content of individual calcite grains in the samples was determined directly with microprobe analysis, which confirmed the data obtained with X-ray diffraction.

#### Dolomite Content

The dolomite content was determined with quantitative X-ray diffraction. As a measure for the dolomite content the area of the 104 reflection was used. A calibration curve was established by adding known amounts of dolomite to a sediment sample. The reproducibility of the analysis varies between 10 and 20%, depending on the dolomite content.

#### Strontium Content

The total strontium content of the sediment samples was determined as part of a study on the occurrence of magnesium, calcium and strontium in argillaceous sediments. The analyses were performed by activation analysis at the RCN (Reactor Centrum Nederland) by Dr. H. A. Das. Additional analyses for this study

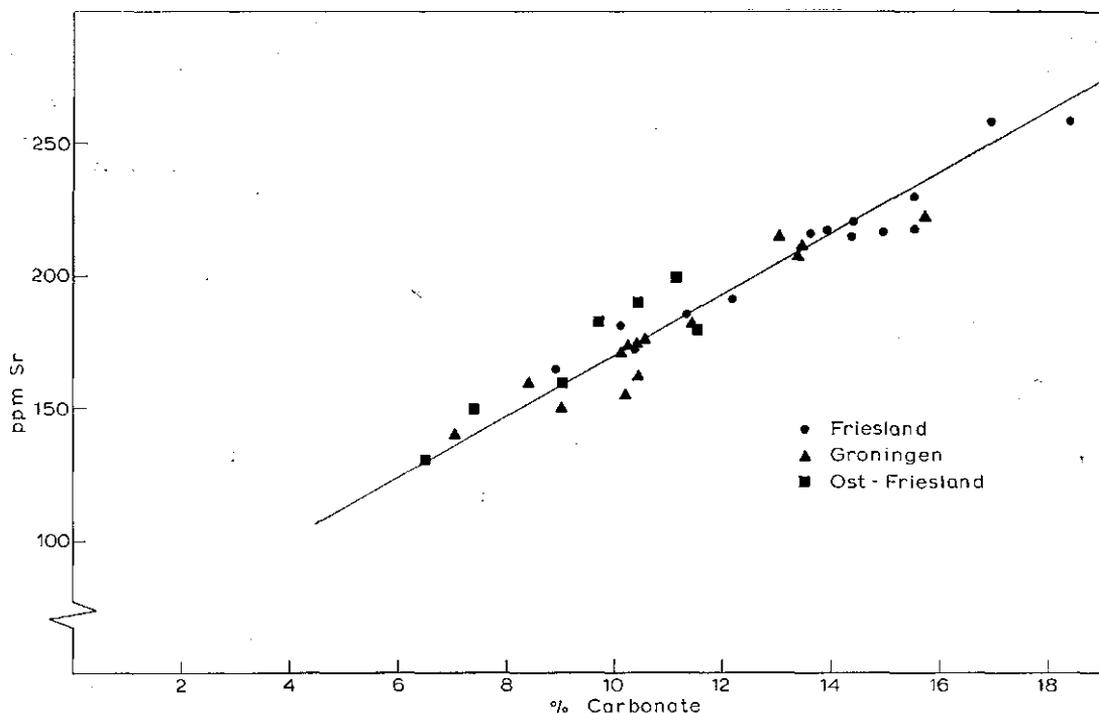


FIG. 3.—Relationship between the total carbonate content and the strontium content for samples from the Wadden area.

were carried out by X-ray fluorescence spectrometry. Details are given by Salomons (1973). In Figure 3 the relationship between the total carbonate content and the total strontium content in sediment samples from the Wadden area is shown. Since part of the strontium is present in the silicates, the curve does not extrapolate through zero. The curve was determined by a least square procedure in order to determine the strontium content of the carbonates.

#### Stable Isotope Analysis

Full details on analytical procedures used can be found in Mook (1968) and Mook and Grootes (1973). Results are given relative to the PDB standard:

$$\delta(\%) = \frac{R_s - R_{st}}{R_{st}} \times 1000$$

$R = {}^{18}\text{O}/{}^{16}\text{O}; {}^{13}\text{C}/{}^{12}\text{C}$   
 $s = \text{sample}$   
 $st = \text{standard}$

The reproducibility of the analysis on pure carbonates is better than 0.1%. Results are based on  $\delta_{\text{PDB}}^{18}$  and  $\delta_{\text{PDB}}^{13}$  values for NBS-20 of -1.06 and -4.14 respectively.

The spread in the isotopic composition of the carbonates in sediment samples from the same locality is about  $\pm 0.3\%$ . For most areas we

made representative samples by mixing a large number of individual samples. This sample was analysed in triplicate.

#### Carbon-14 Content

The carbon-14 analyses were also carried out by the Physics Laboratory of the University Groningen. The carbon-14 content is given in percentages of the NBS oxalic acid standard activity. On this scale recent carbonates formed in the marine environment under natural conditions have a carbon-14 content of about 100%. The carbon-14 content can be used to calculate the age of the sample analysed. However, the carbonates in soils and sediments are generally a mixture of carbonates of various ages, including carbonates with no measurable carbon-14 content at all. Therefore, a calculated C-14 age for these samples is not meaningful. However, the carbon-14 content is a very sensitive parameter to detect the presence of recent carbonates (younger than 50,000 years).

#### Sampling

The sediment samples were taken from the uppermost few millimeters of the deposited material. At each locality at least 20 samples

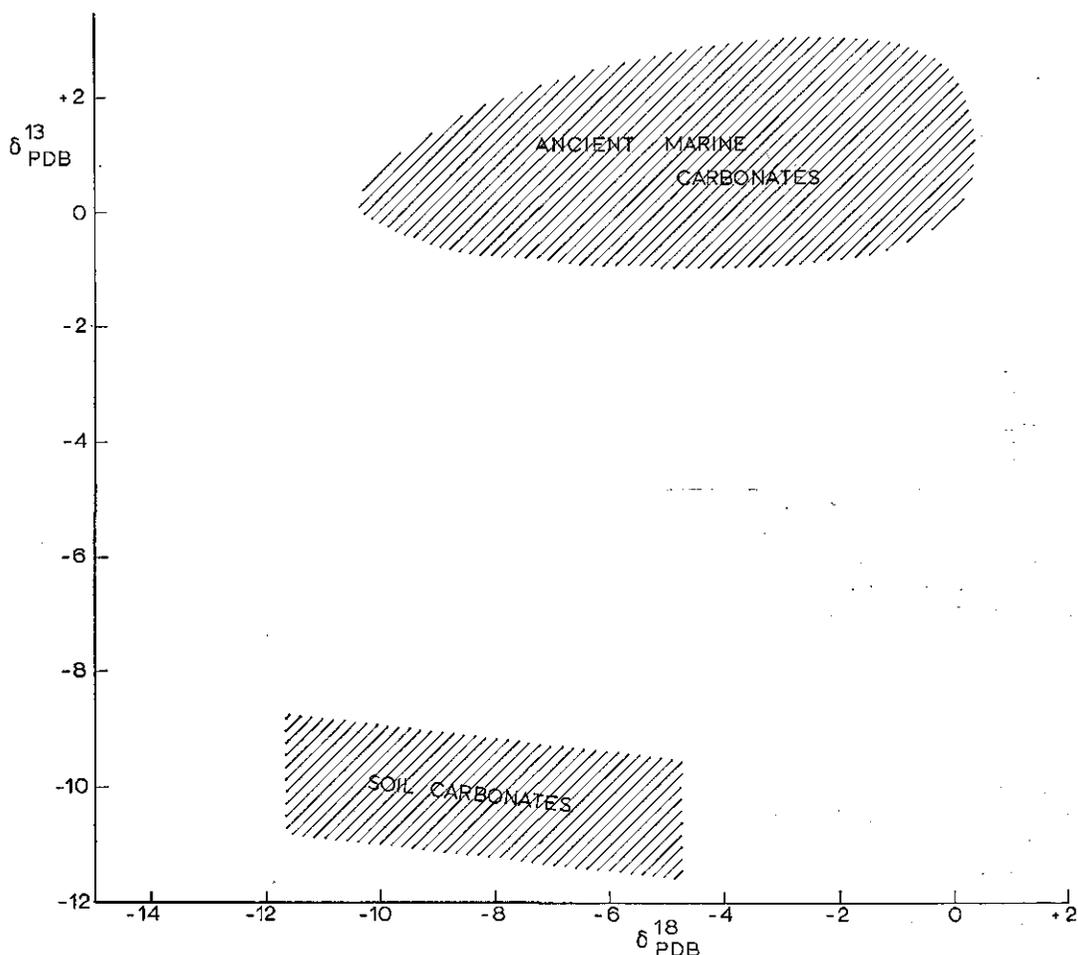


FIG. 4.—The stable isotopic composition of ancient carbonates (Keith and Weber, 1964) and of soil carbonates. The data for the soil carbonates were calculated using the fractionation factors given by Craig (1965) and Emrich *et al.* (1970) for the temperature range of 10–30°C. Oxygen isotopic composition of the groundwater  $-7.5 \pm 1\%$ , carbon isotopic composition of the dissolved bicarbonate  $-12 \pm 1\%$ .

were taken to insure that the whole range in grain sizes from about 20 to 80% particles less than 20 microns is obtained. In some cases the localities were sampled more than once. No significant difference in the composition of the carbonates between the various times of sampling were found.

#### CARBONATES IN SOILS

Soils occur in the first part of the erosion-sedimentation cycle studied. Carbonates in the soil are subject to dissolution which is caused by the high partial pressure of carbon dioxide in the soil atmosphere:



The isotopic composition of carbon dioxide in soils from temperate climates varies between  $-26.5$  and  $-23.5\%$  ( $\delta^{13}_{\text{PDB}}$ ) (Galimov, 1966). If ancient marine carbonate rocks with a carbon isotopic composition of about  $0\%$  (Keith and Weber, 1964) are dissolved, the resulting bicarbonate in the groundwater will have a carbon isotopic composition of about  $-12\%$ . A reprecipitation of the dissolved carbonates takes place deeper in the soil in the form of concretions. Reprecipitation of carbonates in the upper part of the soil is common for soils from semi-arid regions, which often results in the formation of calcrete. On the other hand, knowledge on the processes of reprecipitation in the upper part of soils from temperate climate regions is

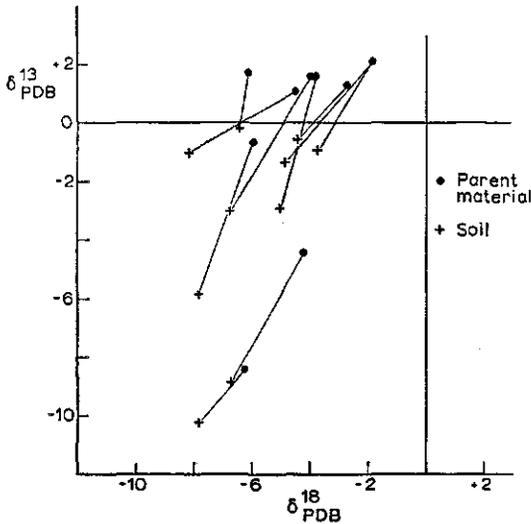


FIG. 5.—Isotopic composition of carbonates in the soil, compared with the isotopic composition of the underlying carbonate rock.

scarce. This part of the soil is important, since it is one of the sources for carbonates in fluvial sediments.

If no reprecipitation takes place, the isotopic composition of the carbonates will be equal to that of the parent material (mostly ancient carbonate rocks). On the other hand if the carbonates are a mixture of parent material and authigenic carbonates, their isotopic composition may comprise the whole range from ancient carbonates to carbonates in equilibrium with groundwater. Especially the carbon isotopic composition is useful to detect the presence of newly formed carbonates (Fig. 4).

#### Soils Developed on Carbonate Rocks

The soils analysed were mainly formed on ancient marine carbonate formations from the Basin of Paris and from the Southern part of the Netherlands. In a few cases soils formed on ancient freshwater carbonate rocks were investigated. The topsoil (0–5 cm) and the parent material were analysed. The carbonates consisted of low-Mg calcite. The isotopic composition of the soil carbonates is in all cases different from that of the parent material (Fig. 5). This shift is caused by the presence of newly formed freshwater carbonates.

The amount of authigenic carbonates can be calculated from the stable carbon isotopic composition. The oxygen isotopic composition is not suitable, because of the seasonal variations

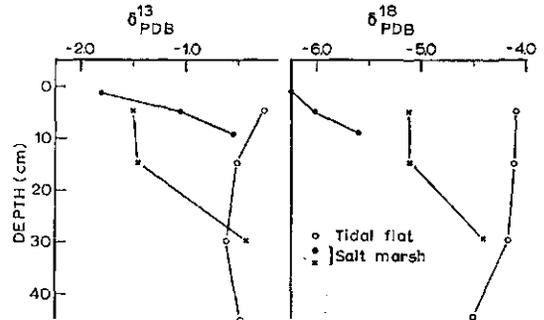


FIG. 6.—The isotopic composition of carbonates in two profiles from the Dollard salt marsh and in one profile from the Dollard tidal flat.

in the isotopic composition of rain water and the large temperature dependence of the fractionation constant between calcite and water. If we assume that the newly formed carbonates are in equilibrium with groundwater, their carbon isotopic composition is about  $-10\%$ . Using this value ( $\delta^{13}(\text{new})$ ) and the carbon isotopic composition of the parent material ( $\delta^{13}(\text{p.m.})$ ), we can calculate the amount of newly formed carbonates using the formula:

$$\% \text{ (newly formed carbonates)} = \frac{\delta^{13}(\text{p.m.}) - \delta^{13}(\text{soil})}{\delta^{13}(\text{p.m.}) - \delta^{13}(\text{new})} \times 100$$

In the soils investigated the amount of newly formed carbonates varies between 10 and 50%.

#### Carbonates in Salt Marshes

The processes affecting carbonates in salt marshes are expected to be similar to the processes occurring in soils. To study the processes in the salt marsh, in as far as they affect the carbonates, we selected the Dollard area. After the last embankment in 1924, the continued sedimentation has resulted in the present salt marsh.

The carbonate content (given at 50% <20 microns) in the surface layers of the salt marsh is about 7%; the value for the tidal flat area is 11% (Table 2). This dissolution of carbonates is also reflected in the calcium content of the pore fluids in the salt marsh sediment.

The mean calcium content of 700 ppm is twice as high as the value found in the tidal flat sediments. Analysis of the carbon isotopic composition of the bicarbonate in the pore fluid showed that the dissolution is caused by the action of biogenic carbon dioxide (Salomons, 1973).

In Figure 6 the isotopic composition of the carbonates in two profiles from the salt marsh

and in one profile from the tidal flat area is given.

In the upper part of the profiles from the salt marsh the isotopic composition is shifted towards negative values. Additionally, we determined the isotopic composition of the carbonates in a large number of samples from the surface layer. The mean value for the carbon isotopic composition is  $-1.7\%$  and for the oxygen isotopic composition is  $-5.6\%$ . Similar values for the tidal flat sediments are  $-0.5\%$  and  $-4.3\%$  respectively (Table 2). Apparently, as in the soils studied, part of the dissolved carbonates are reprecipitated.

#### CARBONATES IN ARGILLACEOUS SEDIMENTS OF RIVERS

The main sources for the carbonates in fluvial sediments from temperate climates are eroded ancient marine carbonate rocks and soils. As we have seen in the foregoing sections, the isotopic composition of carbonates in soils is different from that of ancient carbonate rocks (Figs. 4 and 5).

The data on the carbon isotopic composition indicate that the composition of the river deposits investigated (Table 1) is influenced by

TABLE 1.—The carbonate content (at 50% < 20 microns) and the isotopic composition of carbonates in fluvial sediments

River	Carbonate Content (%)	$\delta^{18}_{PDB}$ (‰)	$\delta^{16}_{PDB}$ (‰)	C-14 (%)
Seine <sup>1</sup>	31.5	-2.1	-4.4	-
Somme <sup>1</sup>	42.0	+0.0	-2.7	-
Rhine	16.0	-3.6	-9.6	14.8
Meuse	5.8	-3.3	-12.6	17.3
Ems	2.5	-5.1	-9.8	33.5
Rhône	-	-1.2	-5.7	-
Humber:Ouse	-	-0.6	-6.8	-
Humber:Trent	-	-0.2	-6.0	-

<sup>1</sup> Carbonate content at 30% < 20 microns.

the supply of pedogenic carbonates to a varying degree. The influence is relatively small in the rivers Ouse, Trent and Somme, but large in the Rhine, Meuse and Seine. Further proof for the presence of carbonates not derived from ancient carbonate rocks is found in the carbon-14 content which is about 15% for the rivers Meuse and Rhine. The carbonates in the river Ems are probably from recent biogenic origin, as is shown by the high strontium content and carbon-14 content (Table 2).

TABLE 2.—Total carbonate content and dolomite content and the composition of the carbonates in argillaceous sediments. The spread in the values of the stable oxygen and carbon isotopic composition is about  $\pm 0.3\%$ . *N* refers to the number of samples analysed,  $\sigma$  to the standard deviation. The total carbonate content is given at 50% < 20  $\mu$ m. The sampled localities from the southern and Wadden area are given in Figure 1. The Rhine-Meuse and the Ems estuary are shown in Figures 9 and 7 respectively.

Locality	Total Carbonate			Dolomite Content			Strontium Content			Isotopic Composition					
	%	N		%	N	$\sigma$	ppm	N	$\sigma$	$\delta^{18}_{PDB}$ (‰)	$\delta^{16}_{PDB}$ (‰)	N	C-14 (%)	$\sigma$ (C-14)	
<i>Southern areas</i>															
Vlaamse Banken	25.7	22		0.7	6	0.1	1300	12	110	+0.3	-2.6	8	31.9	0.3	
Zwarte Polder	20.4	15		0.4	4	0.2	1300	5	110	+0.0	-2.5	4	-	-	
Grevelingen	20.2	19		1.0	5	0.2	1300	9	110	-0.5	-3.2	5	43.7	0.5	
<i>Rhine-Meuse estuary</i>															
Oost-Biesbosch	5.8	14		0.9	5	0.4	850	10	140	-3.3	-12.6	3	17.3	0.4	
Dordtse Biesbosch	16.0	20		2.1	7	0.2	850	14	140	-3.6	-9.6	8	14.8	0.3	
Hollands Diep 1										-2.0	-8.7	3	-	-	
Hollands Diep 2	12.0	43		0.9	5	0.2	950	6	150	-1.3	-7.0	3	-	-	
Hollands Diep 3										-1.2	-6.4	2	-	-	
Haringvliet	19.3	33		1.5	7	0.4	1150	15	130	-0.6	-4.5	4	29.3	0.3	
Brielsche Gat	19.5	21		1.2	7	0.2	-	-	-	-0.6	-3.8	5	-	-	
<i>Wadden Sea Area</i>															
Friesland	16.9	57		1.3	24	0.4	1100	14	60	-0.5	-3.6	4	22.2	0.4	
Groningen	11.7	18		1.3	6	0.4	1100	16	60	-0.1	-4.0	9	28.6	0.4	
Dollard	10.4	18		1.4	9	0.3	1100	20	60	-0.5	-4.3	12	15.7	0.4	
Ost Friesland	11.0	18		-	-	-	1100	7	60	-0.4	-3.4	5	30.6	0.5	
<i>Ems estuary</i>															
Diele	2.5	14		0.4	5	0.1	5600	12	600	-5.0	-9.8	2	33.5	0.6	
Leerort	7.0	18		1.2	5	0.2	1350	19	160	-0.6	-5.6	3	-	-	
Ditzum	10.0	14		1.4	4	0.3	1100	8	120	-0.5	-5.0	3	-	-	

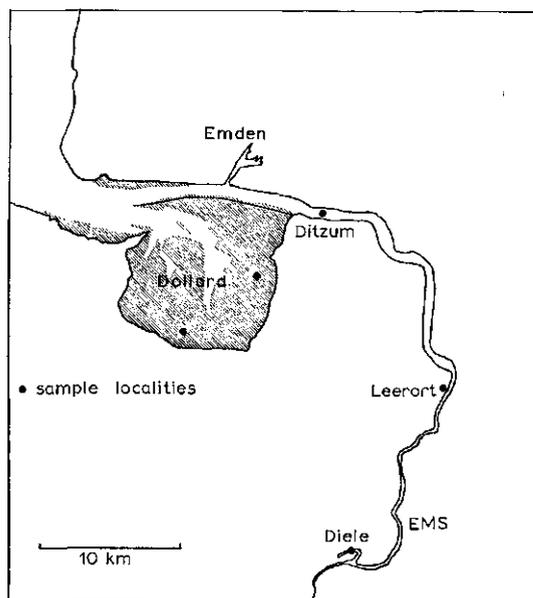


FIG. 7.—The estuary of the river Ems.

#### CARBONATES IN ESTUARINE ARGILLACEOUS SEDIMENTS

The next part of the erosion-sedimentation cycle studied is located in the estuaries. There we have the transition from the fluvial to the marine environment, the sediments being mixtures in various proportions of material supplied from both directions. In the next sections we will discuss the comparatively small Ems-estuary and the Rhine-Meuse estuary.

#### *The Ems-Estuary*

The Ems estuary (Fig. 7) is a relatively small river, compared to the river Rhine. The average discharge of water is 100 m<sup>3</sup>/sec (Dorrestein, 1960). The mud discharge is estimated at  $0.14 \times 10^6$  ton/year (McCave, 1973).

The freshwater sediments were sampled at Diele, the estuarine deposits at Leerort and Ditzum. The chlorinity of the water at Leerort varies between 0 and 1‰, at Ditzum between 1 and 7‰. The carbonates in the sediments were

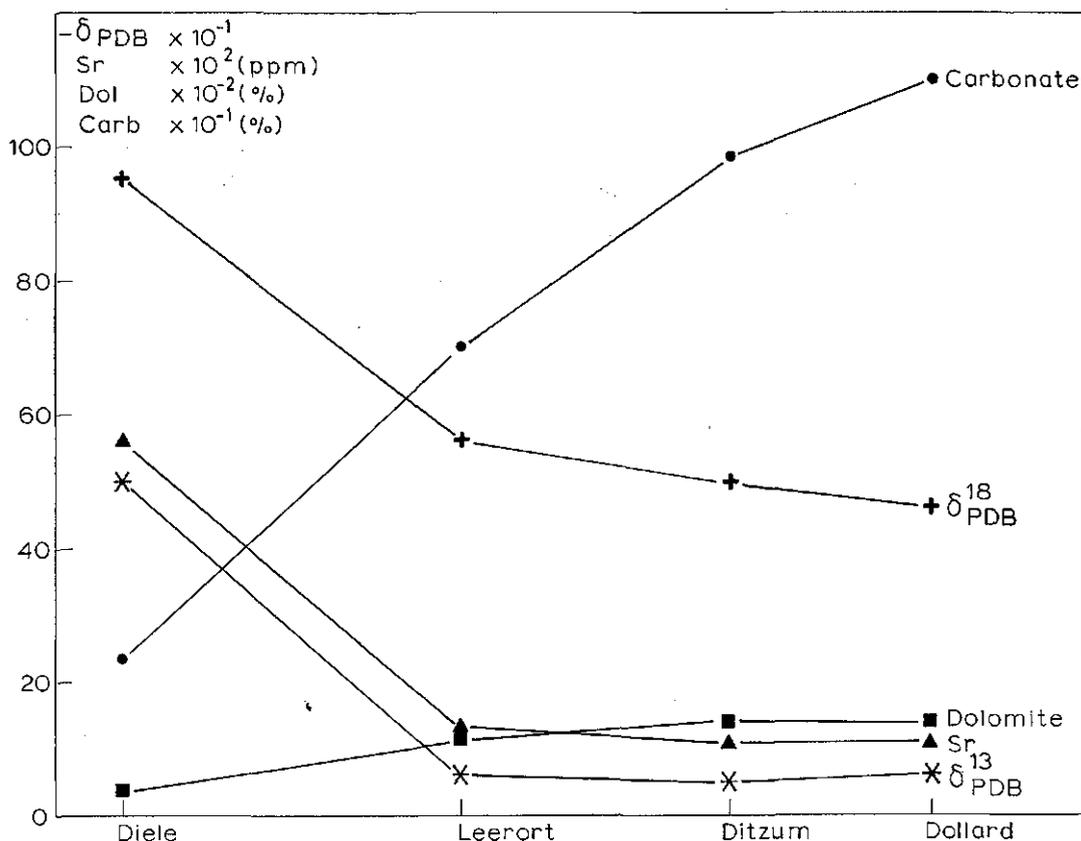


FIG. 8.—Total carbonate content, dolomite content and the composition of the carbonates in Ems sediments.

examined by X-ray diffraction and found to consist of low-Mg calcite and dolomite. The magnesium content of the calcite is below 1%.

The total carbonate content and dolomite content of the sediments increase in seaward direction (Table 2). Apparently, the carbonates deposited in the estuary are only partly of fluvial origin. The strongest change in the composition of the carbonates is found at Leerort (Fig. 8). At Ditzum it is already comparable to that in marine deposits of the Dollard area. We may conclude from these data that the progressive change in the composition of the carbonates in seaward direction is caused by mixing of marine and fluvial carbonates. The strontium content can be used as a sensitive parameter to determine the amount of marine carbonates in the Ems-estuary. At Leerort where the chlorinity of the water is about 1‰, already 90% of the carbonates deposited are of marine origin. Such a discrepancy between chlorinity of the water and carbonate composition of the sediments was also found in the Rhine-Meuse estuary.

#### *The Rhine-Meuse Estuary*

The estuarine and river samples were sampled before the closure of the Haringvliet and the Grevelingen. At present the discharge of river water from the Rhine and Meuse is mainly through the Nieuwe Waterweg to the North Sea.

The main mud discharge takes place through the Haringvliet whereas not more than 10% of the mud is discharged through the Krammer (Terwindt, 1967). The marine mud originates from the area south of the estuary and is transported in a northern direction along the Belgian and Dutch coast.

Freshwater sediment samples from the river Rhine were sampled in the Dordtsche Biesbosch, freshwater samples from the Meuse in the Oost-Biesbosch (Fig. 9). Estuarine sediments were sampled in the Hollands Diep, Haringvliet and Brielse Gat. The Hollands Diep is comparable to the Ems between Leerort and Ditzum with regard to the chlorinity of the water. Only on the southern side of the Hollands Diep are conditions favourable for the intertidal deposition of mud.

The carbonates in the sediments investigated consisted of low-Mg calcite (Mg content <1%) and dolomite. In the estuary the total carbonate and dolomite contents in the sediments as well as the composition of the carbonates change in seaward direction (Table 2). For the Rhine-

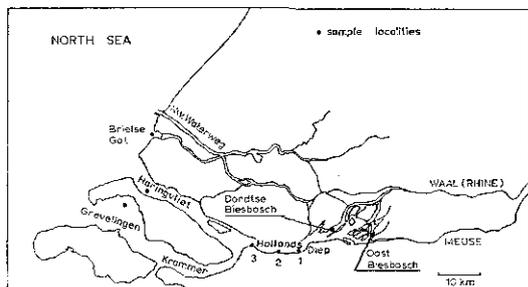


FIG. 9.—The Rhine-Meuse estuary.

Meuse estuary the most sensitive parameter to determine the ratio of fluvial to marine carbonates is their isotopic composition. Since the oxygen isotopic composition for the Rhine differs from that for the Meuse, we will use mainly the carbon isotopic composition. In this calculation the carbon isotopic composition of fluvial carbonates is taken as  $-3.6\text{‰}$  and of marine carbonates as  $+0.3\text{‰}$ .

From the total carbonate content in the Hollands Diep one could assume that a mixing of Rhine with Meuse material takes place, resulting in a carbonate content of 12%. However, the carbon isotopic composition indicates that we have a mixing of marine and fluvial carbonates; more than 40% of the carbonates being derived from the marine environment. The total carbonate content and the oxygen isotopic composition can be used to differentiate between carbonates from the rivers Rhine and Meuse. If we assume that in the Hollands Diep a mixing of Rhine sediments with marine sediments takes place in a ratio of 1:1, the oxygen isotopic composition of the carbonates in the Hollands Diep should be about  $-4.6\text{‰}$  and the total carbonate content of the sediments about 18%. The values found show that this is not the case. A similar calculation for a mixing of Meuse and marine sediments gives a total carbonate content of the sediment of 13% and an oxygen isotopic composition of about  $-6\text{‰}$ , which corresponds rather well with the values found; respectively 12% for the total carbonate content and  $-7\text{‰}$  for the oxygen isotopic composition. In the Hollands Diep very little mixing of Rhine and Meuse sediments is observed.

The carbonates deposited in the Haringvliet are derived for about 70% from the marine environment. The stable oxygen isotopic composition, the strontium content and the carbon-14 content of the carbonates all fit in with such a strong marine influence.

TABLE 3.—*The amount of suspended matter transported annually in the area studied*

Source	Supply ( $\times 10^6$ ton)
Rhine-Waal <sup>1</sup>	3.20
Meuse <sup>1</sup>	0.70
English Channel <sup>2</sup>	5.10
Scheldt <sup>2</sup>	0.40
Ems <sup>2</sup>	0.14

<sup>1</sup> After Terwindt (1967).

<sup>2</sup> After McCave (1973).

In the present estuary, the Rotterdam harbour and Nieuwe Waterweg the same strong influence on the composition of the carbonates is found (Salomons, 1973). This landward transport of sediments in an estuary has been described by Meade (1969) and by Postma (1967).

#### CARBONATES IN MARINE ARGILLACEOUS SEDIMENTS

Possible sources for the carbonates in marine sediments are: fluviatile carbonates, carbonates derived from eroded carbonate formations along the coast and recent biogenic carbonates.

Data on the present-day sources for the suspended matter in the area studied are given in Table 3.

Although the amount of suspended matter transported through the English Channel is large, its concentration in the water is low, it is transported in a northerly direction along the Belgian and Dutch coast. Sediments from this source are found at the localities 3, 4 and 5 (Fig. 1). North of the Rhine-Meuse estuary large amounts of suspended matter from the rivers Rhine and Meuse are added to this material. Part of the suspended matter is transported to the Wadden area, where an extensive accumulation of mud takes place (van Straaten, 1954; van Straaten and Kuenen, 1957). The finely grained carbonates in this area are therefore mainly derived from the area south of the Rhine-Meuse estuary and from the

rivers Rhine and Meuse. Furthermore, during transport and after deposition the addition of recent carbonates has to be taken into account. This causes the presence of aragonite and high-Mg calcite both with a high carbon-14 content. Yet, no aragonite could be detected. Apparently, crushed remains of aragonitic shells like *Cardium* and *Mytilus*, which occur abundantly in the area investigated, are not an important source for the carbonates in these finely grained sediments. Furthermore, the composition of the carbonates in the Wadden area is consistent with a mixture of Rhine-Meuse carbonates and carbonates derived from the southern areas (Table 4). It follows that the addition of recent carbonates during transport along the Dutch coast and in the Wadden Sea is small compared to the amount of detrital carbonates present.

Using the data in Table 4 a rough estimate can be made on the amount of fluviatile carbonates present. About one fifth of the carbonates are derived from the rivers Rhine and Meuse, the remainder originate from the southern areas. The fluviatile carbonates from the river Ems, with their high Sr-content, have no measurable influence on the composition of the carbonates found in the Wadden area.

#### CONCLUSIONS

- (1) Part of the dissolved carbonates in soils from temperate climates are reprecipitated in the upper part of the soil.
- (2) The carbonates in argillaceous sediments from the rivers Rhine, Meuse, Seine and Rhône are partly derived from soils. The carbonates in the river Somme are derived from eroded carbonate rocks.
- (3) The carbonates in the estuaries of the rivers Rhine, Meuse and Ems are mainly derived from the marine environment.
- (4) The carbonates in the marine argillaceous sediments from the Wadden area are for about one fifth derived from the rivers Rhine and Meuse.

TABLE 4.—*Mean values for the total carbonate content and the composition of the carbonates in the main areas*

Area	Total Carbonate Content (%)	Strontium Content (ppm)	$\delta^{18}_{\text{PDB}}$ (‰)	$\delta^{13}_{\text{PDB}}$ (‰)	C-14 (%)
Southern Areas	22	1300	-0.1	- 2.8	38
Rhine-Meuse	13	850	-3.5	-11.1	16
Wadden Sea Area	12	1100	-0.4	- 3.8	24
Ems	3	5600	-5.0	- 9.8	33

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